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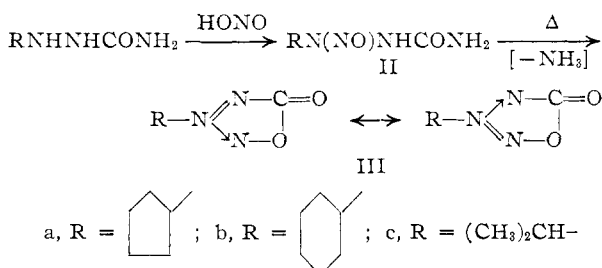
Properties of Alkyl and Aryl- ψ -oxatriazoles¹BY J. H. BOYER AND J. A. HERNANDEZ²

RECEIVED MAY 28, 1956

Heating 1-cyclopentyl-, 1-cyclohexyl- and 1-isopropyl-1-nitrososemicarbazides in dilute hydrochloric acid which also contained nitrous acid brought about the formation of the corresponding alkyl- ψ -oxatriazoles. A similar attempt to prepare benzyl- ψ -oxatriazole led to an unidentified liquid. Four aryl- ψ -oxatriazoles prepared from the corresponding arylazotrinitromethane and the alkyl- ψ -oxatriazoles absorbed in the infrared at 1800 and 1760 cm^{-1} , respectively, indicative of a carbonyl group in a five-membered ring. Cyclohexanol was obtained in good yield upon acid hydrolysis of cyclohexyl- ψ -oxatriazole.

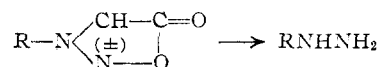
It was suggested that N-nitrososemicarbazides (II) were intermediates in the transformation of alkyl semicarbazides (I) into the corresponding alkyl- ψ -oxatriazoles by the action of nitrous acid.³ The isolation of such intermediates has now been realized at low temperatures.

Upon warming dilute acid solutions of nitrososemicarbazides, products from at least three different reaction paths have been observed. The aryl nitrososemicarbazides were transformed into arylazocarboxamides, apparently with the elimination of nitroxyl.³ Alkyl nitrososemicarbazides underwent the loss of ammonia, or its equivalent, with the formation of alkyl- ψ -oxatriazoles (III). Hydrolysis of benzyl nitrososemicarbazide was reported; however, the suspected products, benzyl alcohol and carbamyl azide, were not isolated.⁴ Carbamyl azide has now been obtained in trace amounts from the transformation of isopropyl nitrososemicarbazide into isopropyl- ψ -oxatriazole; however, isopropyl alcohol was not detected.



Hydrolysis of alkyl- ψ -oxatriazoles has now been observed under more drastic conditions. Cyclohexyl- ψ -oxatriazole resisted attack by dilute mineral acid and was precipitated from solution by the addition of sulfuric acid. Upon treatment with more concentrated sulfuric acid (about 75%) at higher temperatures (about 80°), the evolution of carbon dioxide and hydrogen azide was detected, and cyclohexanol was isolated in good yield. That cyclohexyl azide was not detected is not in agreement with the reported hydrolysis of phenyl- ψ -oxatriazole in sulfuric acid. In this case the evolution of carbon dioxide and the formation of phenyl azide was claimed.⁵ There is a sharp contrast between the behavior of the ψ -oxatriazoles and the isosteric

sydnones (IV) toward strong acid. The latter are transformed into the corresponding alkyl and aryl-hydrazines.⁶



Four aryl- ψ -oxatriazoles were prepared from the corresponding arylazotrinitromethane.⁵ Strong absorption in the infrared at 1800 cm^{-1} (carbonyl in a five-membered ring) and no absorption at 2175–2225 cm^{-1} (cyanate group) was characteristic of each. This together with a negative Liebermann nitroso test and resistance to hydrolysis supported Ponzio's oxatriazole assignment.⁷

Experimental⁸

Reduction of Semicarbazones.—Poth and Bailey's procedure⁹ was followed for the catalytic reduction of the semicarbazones. Phenylsemicarbazide was commercially available. Cyclohexylsemicarbazide, m.p. 179°¹⁰ (85%), benzylsemicarbazide, m.p. 155.5°⁴ (65%), and isopropylsemicarbazide, m.p. 127–129°¹¹ (90%), were obtained upon reduction of the corresponding semicarbazones.

Preparation of 1-Nitrososemicarbazides.—To a solution or slurry of 0.10 mole of the substituted semicarbazide in 30 ml. of hydrochloric acid and 30 ml. of water cooled to –20° in the Dry Ice and acetone-bath, was added with stirring 100 ml. of 15% sodium nitrite solution dropwise so that the temperature of the reaction mixture did not rise above –15°. After all of the sodium nitrite solution had been added, the cooling bath was replaced by a 40° water-bath, 20 ml. of *n*-octyl alcohol as an antifoaming agent was added, and the mixture was stirred vigorously until the evolution of nitrogen oxides had ceased. The crude nitrososemicarbazides were collected by filtration and recrystallized from aqueous alcohol. Phenylazocarboxamide, m.p. 114°,¹² was obtained in 60% yield from phenyl semicarbazide. From 1-cyclohexylsemicarbazide, 1-nitroso-1-cyclohexylsemicarbazide, m.p. 129–130°, was obtained in 70% yield.

Anal. Calcd. for $\text{C}_7\text{H}_{14}\text{N}_4\text{O}_2$: C, 45.16; H, 7.73; N, 30.10. Found: C, 45.25; H, 7.64; N, 29.84.

From 1-cyclopentylsemicarbazide, the 1-nitroso derivative, m.p. 117–118°, was obtained in 75% yield.

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{N}_4\text{O}_2$: C, 41.86; H, 6.97; N, 32.56. Found: C, 41.89; H, 6.90; N, 32.50.

(6) J. M. Tien and I. M. Hunsberger, *THIS JOURNAL*, **77**, 8604 (1955).

(7) G. Ponzio, *Gazz. chim. ital.*, **63**, 471 (1933). These properties suggest that the formulation of these molecules as open chain aryl nitroso carbonylhydrazines (Z. E. Jolles, "Nitrogen Derivatives of Aniline," Chapter VI, "Chemistry of Carbon Compounds," Vol. IIIA, Elsevier Publishing Company, Houston, Texas, 1954, p. 342) is misleading.

(8) Melting points are corrected. Elemental analyses by Microtech Laboratory, Skokie, Ill. Infrared analyses by Mr. J. E. Baudean, Perkin-Elmer Corp., New Orleans, La.

(9) E. J. Poth and J. R. Bailey, *THIS JOURNAL*, **45**, 3001 (1923).

(10) A. I. Vogel, *J. Chem. Soc.*, 721 (1929).

(11) D. W. Neighbors, A. L. Foster, S. M. Clark, J. E. Miller and J. R. Bailey, *THIS JOURNAL*, **44**, 1557 (1922).

(12) O. Widman, *Ber.*, **28**, 1925 (1895).

(1) Partial support of this work under Office of Ordnance Research, U. S. Army Contract No. DA-01-009-ORD-428 is gratefully acknowledged.

(2) Recipient of a Venezuelan Government Fellowship, 1954–1955, and a Creole Petroleum Corporation fellowship 1955–1956.

(3) J. H. Boyer and F. C. Canter, *THIS JOURNAL*, **77**, 1280 (1955).

(4) S. Kessler and H. Rupe, *Ber.*, **45**, 26 (1912).

(5) A. Quilico, *Gazz. chim. ital.*, **62**, 912 (1932).

From 1-benzylsemicarbazide, the 1-nitroso derivative, m.p. 133°,⁴ was obtained in 75% yield.

Anal. Calcd. for C₈H₁₀N₄O₂: C, 49.48; H, 5.18; N, 28.85. Found: C, 49.68; H, 5.47; N, 28.56.

Attempts to isolate 1-isopropyl-1-nitrososemicarbazide were unsuccessful; however, an unstable low melting intermediate solid was observed. This solid in agreement with the above N-nitroso compounds gave a positive Liebermann nitroso test. These observations on the stability of 1-isopropyl-1-nitrososemicarbazide are not in agreement with an earlier claim that the compound had a m.p. of 128°¹¹ (probably unreacted isopropylsemicarbazide, m.p. 128°). Elemental analysis was not reported.

Preparation of Alkyl- ψ -oxatriazoles.—Boyer and Canter's procedure³ was used with the modification of a wider temperature range. A solution or slurry of a semicarbazide in 30 cc. of water and 30 cc. of concentrated hydrochloric acid was cooled to -20° in a Dry Ice and acetone-bath. With stirring, 100 cc. of 15% sodium nitrite solution was added, the cooling bath was replaced by a 60° water-bath, and the material was stirred vigorously until evolution of nitrogen oxides had ceased. Ether extracts of the cooled solution were washed with dilute ammonium hydroxide solution and then with water, dried over anhydrous magnesium sulfate, and then removed by distillation at reduced pressure. In each case the residue was purified by further distillation or recrystallization. Cyclohexyl- ψ -oxatriazole (56%) recrystallized from ether-acetone-water as colorless needles, m.p. 73.2°.

Anal. Calcd. for C₇H₁₁N₃O₂: C, 49.69; H, 6.55; N, 24.82. Found: C, 49.96; H, 6.97; N, 24.91.

Cyclopentyl- ψ -oxatriazole (58.5%) distilled at 92-95° (0.25-0.30 mm.), *n*_D²⁰ 1.4950. Upon redistillation an analytical sample, *n*_D²⁰ 1.4959, b.p. 65° (0.06 mm.), was obtained.

Anal. Calcd. for C₆H₉N₃O₂: C, 46.39; H, 6.04; N, 27.68. Found: C, 46.52; H, 5.73; N, 27.80.

When the reaction with cyclopentylsemicarbazide was run at lower temperature (-50°), and the cold material was extracted with ether and recrystallized from acetone, a crystalline product, m.p. 187.5-187.7° with decomposition at 190°, was obtained in low yield. The analytical data suggested that it was a dicyclopentylsemicarbazide.

Anal. Calcd. for C₁₁H₂₁N₃O: C, 62.56; H, 10.05; N, 19.91. Found: C, 63.24; H, 10.14; N, 20.17.

When the reaction with cyclopentylsemicarbazide was run at -15°, the product of the reaction, a pale yellow solid material, was separated and washed with distilled water. As it was being dried under vacuum, it exploded.

Isopropyl- ψ -oxatriazole (67.5%) distilled at 60-61.5° (0.045-0.050 mm.), *n*_D²⁰ 1.4594.

Anal. Calcd. for C₄H₇N₃O₂: C, 37.20; H, 5.46; N, 32.55. Found: C, 37.37; H, 5.49; N, 32.85.

Distillation of crude isopropyl- ψ -oxatriazole allowed traces of solid carbamylazide to separate in the condenser. This was purified by sublimation at 75° (0.08 mm.), and was recrystallized from ethanol from which it separated as colorless crystals, m.p. 97-98°.¹³ Strong infrared absorption at 2160 and at 1725 cm.⁻¹ indicated the presence of the azido and carbonyl groups, respectively.

Attempts to prepare benzyl- ψ -oxatriazole led to the formation of an unidentified clear colorless viscous liquid, *n*_D²⁰ 1.5356, b.p. 59° (1.8 mm.).

Anal. Calcd. for C₁₉H₁₈N₃O: C, 68.28; H, 5.42; N, 21.08. Found: C, 68.23; H, 5.59; N, 21.61.

Attempts to prepare phenyl- ψ -oxatriazole from phenyl-

semicarbazide led to the formation of slightly yellow crystalline phenylazocarboxamide, m.p. 114°,¹² upon recrystallization from benzene. Nitrosation at -20° allowed the detection (positive Liebermann nitroso test) of an intermediate nitroso compound. It was not possible to isolate this unstable intermediate. Upon recrystallization from water, phenylazocarboxamide separated as an unstable hydrate, dec. at 85°, which upon further recrystallization from benzene separated as the anhydrous phenylazocarboxamide, m.p. 114°.

Anal. Calcd. for C₇H₇N₃O: C, 56.38; H, 4.70; N, 28.18. Found: C, 56.20; H, 4.76; N, 28.02.

Acid Decomposition of Cyclohexyl- ψ -oxatriazole.—To a 20-cc. solution of 80% sulfuric acid at 75° was added portionwise with shaking 4.47 g. of cyclohexyl- ψ -oxatriazole. A tremendous evolution of gas followed and was found to contain carbon dioxide and hydrazoic acid. After all the solid was added the mixture was diluted with 60 cc. of cold water and extracted with ether. The ether extract was washed with water and evaporated at reduced pressure. The residue, identified as cyclohexanol, was cooled and 2.2 g. of an oily material was obtained. Upon further distillation at reduced pressure 1.6 g. (60.6%) of a clear colorless liquid b.p. 69-70° (21 mm.), *n*_D²⁰ 1.4615, was obtained and redistilled, b.p. 65° (16 mm.), *n*_D²⁰ 1.4625.

Anal. Calcd. for C₆H₁₂O: C, 71.95; H, 12.07. Found: C, 71.42; H, 12.02.

The m.p. and mixed m.p. with cyclohexyl 3,5-dinitrobenzoate was 111.6-112.2°.

Preparation of Aryl- ψ -oxatriazoles.—Quilico's procedure⁵ with minor variations was used and is demonstrated by the preparation of the previously unreported 2-nitro-3-methylphenyl- ψ -oxatriazole.

The diazonium chloride solution obtained upon the diazotization of 1.52 g. (0.01 mole) of 3-nitro-4-aminotoluene was added dropwise to a solution of 1.7 g. (0.01 mole) of ammonium nitroformate⁵ in 50 ml. of water which also contained 2.0 g. of sodium acetate. Both reactants were kept at 0° during the addition period. The precipitation of a yellow microcrystalline solid commenced immediately. After separation by filtration, thorough washing with cold water and drying in a desiccator this product, 3-nitro-4-toluenediazonium nitroformate, was obtained in 35% yield (1.1 g.), m.p. 72.5-73° dec. A solution of 2.5 g. (0.008 mole) of this diazonium nitroformate in 10 ml. of glacial acetic acid was maintained at 60-65° until the evolution of nitrogen oxides ceased. Upon the addition of 100 ml. of cold water, the slightly yellow 2-nitro-3-methylphenyl- ψ -oxatriazole precipitated, 1.32 g. (74%), m.p. 138-139°. After three recrystallizations from alcohol the yellow color persisted and the melting point became constant at 141-141.5°.

Anal. Calcd. for C₈H₈N₄O₄: C, 43.25; H, 2.72; N, 25.22. Found: C, 42.92; H, 2.79; N, 25.12.

This procedure was then followed for the transformation of *p*-bromoaniline into *p*-bromophenyldiazonium nitroformate, m.p. 70° dec.,¹⁴ and *p*-bromophenyl- ψ -oxatriazole, m.p. 145°⁵; *p*-chloroaniline into *p*-chlorophenyldiazonium nitroformate, m.p. 68.5° dec.¹⁴ and *p*-chlorophenyl- ψ -oxatriazole, m.p. 133°⁵; *p*-nitroaniline into *p*-nitrophenyldiazonium nitroformate, m.p. 61-62° dec.,¹⁴ and *p*-nitrophenyl- ψ -oxatriazole, m.p. 166°.⁵ Each of these four aryl ψ -oxatriazoles absorbed in the infrared at 1800 cm.⁻¹.

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(14) A. Quilico⁵ reported *p*-chlorophenyldiazonium nitroformate, m.p. 68° dec., and observed that *p*-bromophenyldiazonium nitroformate and *p*-nitrophenyldiazonium nitroformate exploded upon heating but gave no specific temperature for the decomposition.

(13) J. Thiele and O. Stange, *Ann.*, **283**, 374 (1894).